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[Claim(s)]

[Claim 1] At least, an electrode is laminated on one field of one substrate, and a semiconductor layer is laminated on the surface of this electrode, In an optoelectric transducer by which a counter-electrode is laminated on one field of a substrate of another side, it is arranged so that said semiconductor layer may stand face to face against said counter-electrode, and an electrolyte layer is further allocated between said semiconductor layer and said counter-electrode, An optoelectric transducer, wherein at least a part of the optoelectric-transducer components other than said substrate and an electrolyte layer has a slanting columnar structure and a crevice exists between these slanting columnar structures.

[Claim 2] The optoelectric transducer according to claim 1 which allocating an insulating layer which has a slanting columnar structure between said semiconductor layer and a counter-electrode, and a crevice's existing between these slanting columnar structures, and impregnating in an electrolyte in this crevice.

[Claim 3] The optoelectric transducer according to claim 1, whercin said semiconductor layer has a slanting columnar structure, a crevice exists between these slanting columnar structures and sensitizing dye is supported

in this crevice.

[Claim 4]The optoelectric transducer according to any one of claims 1 to 3, wherein an angle of inclination of said columnar structure is changing gradually.

[Claim 5]The optoelectric transducer according to claim 2, wherein a catalyst bed is further allocated between a counter-electrode conductive layer and said insulating layer.

[Claim 6]The optoelectric transducer according to claim 3, wherein a center section of an aslant inclined columnar structure mainly comprises a conductive substance in said semiconductor layer and the surface portion mainly comprises semi-conducting material.

[Claim 7]The optoelectric transducer according to claim 1, wherein an aslant inclined columnar structure thing comprises polycrystal.

[Claim 8]The optoelectric transducer according to claim 1, wherein a substrate by the side of a work electrode is a flexible base at least.

[Claim 9]At least, an electrode is laminated on one field of one substrate, and a semiconductor layer is laminated on the surface of this electrode, In a manufacturing method of an optoelectric transducer with which a counter-electrode is laminated on one field of a substrate of another side, it is arranged so that said semiconductor layer may stand face to face against said counter-electrode, and an electrolyte layer is further allocated between said semiconductor layer and said counter-electrode, A manufacturing method of an optoelectric transducer forming at least a part of the optoelectric-transducer components other than said substrate and an electrolyte layer with vacuum deposition.

[Claim 10]A manufacturing method of the optoelectric transducer according to claim 9, wherein evaporation vapor enters aslant to a substrate.

[Claim 11]A manufacturing method of the optoelectric transducer according to claim 9 forming membranes continuously rolling round a long picture flexible

base.

[Claim 12]A manufacturing method of the optoelectric transducer according to claim 9 forming said semiconductor layer by the ion plating method.

[Claim 13]A manufacturing method of the optoelectric transducer according to claim 9 forming said semiconductor layer with a vacuum deposition method which used ion beam irradiation together.

[Claim 14]A manufacturing method of the optoelectric transducer according to claim 9 characterized by performing plasma treatment after forming said semiconductor layer with a vacuum deposition method.

[Claim 15]A manufacturing method of the optoelectric transducer according to claim 9 characterized by performing a hotpress after forming said semiconductor layer with a vacuum deposition method.

[Detailed Description of the [Invention]]

[0001]

[Field of the Invention]This invention relates to an optoelectric transducer. More particularly, this invention has a low resistance loss and low transmission loss, and relates to the optoelectric transducer of a new structure where high photoelectric conversion efficiency can be attained.

[0002]

[Description of the Prior Art]The solar cell is greatly expected as a clean energy source, and the pn junction type solar cell etc. are already put in practical use. On the other hand, although the photogalvanic cell which takes out electrical energy using the chemical reaction of a photoexcited state was developed by many researchers, when saying about utilization, it was already in Haruka at the high pn junction type solar cell of the track record.

[0003]The type which used the oxidation-reduction reaction which consists of a sensitizer and an electron acceptor in the conventional photogalvanic cell is known. For example, there are a system etc. which combined thionine

dye and iron (II) ion. The photogalvanic cell using the photocharge separation of metal or its oxide has also been known since discovery of the Honda-Fujishima effect. When a semiconductor contacts metal, the Schottky barrier is made with the relation of the work function of metal and a semiconductor, but same junction can be performed also when the semiconductor and the solution have touched. In a solution, for example, $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$. When redox systems, such as I^-/I_2 , Br^-/Br_2 , hydroquinone/quinone, are included, if n type semiconductor is soaked in a solution, the electron near the surface of a semiconductor will move to the oxidizer in a solution, and will reach an equilibrium situation. As a result, near the surface of a semiconductor is just charged and an electric potential gradient produces it. In connection with this, inclination arises also in the conducting zone and valence band of a semiconductor.

[0004] If the surface of the semiconductor electrode soaked in the oxidation reduction solution is irradiated, light with the energy more than the band gap of a semiconductor is absorbed, and near the surface, an electron will be generated to a conducting zone and it will generate an electron hole to a valence band. The electron excited by the conducting zone is transmitted to the inside of a semiconductor by the electric potential gradient which exists near the surface of the semiconductor mentioned above, and, on the other hand, the electron hole generated by the valence band takes an electron from the reduced form in a oxidation reduction solution.

[0005] If a metal electrode is dipped in a oxidation reduction solution and a circuit is made between a metal electrode and a semiconductor, the reduced form from which the electron was taken in the electron hole will diffuse the inside of a solution, will receive an electron from a metal electrode, and will be returned again. This cycle is repeatable, a semiconductor electrode can be committed as an anode, a metal electrode can be committed as a cathode, respectively, and electric power can be supplied to the exterior. Therefore,

photoelectromotive force becomes a difference of the oxidation reduction level of a oxidation reduction solution, and the Fermi level in a semiconductor.

[0006]In order to enlarge photoelectromotive force, it is using the strong oxidation reduction solution of oxidizing power low [** oxidation reduction level], and being able to make a big difference, namely, using a semiconductor with a large band gap between ** oxidation reduction level and the Fermi level in a semiconductor.

[0007]However, if the oxidizing power of a oxidation reduction solution is too large not much, an oxide film is formed in a semiconductor's own surface, and photoelectric current is stopped in the inside of a short time. Generally about a band gap, there is a problem which a band gap tends to dissolve into a solution by the current through which 3.0-eV or less a semiconductor of 2.0 more eV or less flows in the case of photoelectric conversion. For example, n-Si forms an inertness oxide film in the surface by underwater optical exposure, and n-GaAs and n-CdS dissolve oxidatively.

[0008]The device which covers a protective film is tried by the semiconductor in these problems at the ***** sake, and the device which uses p type conductive polymers which have electron hole transport properties, such as polypyrrole, poly aniline, and a polythiophene, for the protective film of a semiconductor is proposed. However, there is a problem in endurance and it was stabilized only about several days at most.

[0009]In order to solve the problem of the optical dissolution, use of a semiconductor with not less than 3 eV of band gaps can be considered. but a strong peak is too large for absorbing the sunlight near 2.5 eV efficiently. Therefore, only an ultraviolet region can be absorbed among sunlight, and the visible range which occupies most is not absorbed at all, but photoelectric conversion efficiency becomes very low.

[0010]In order to reconcile effective use of a light region, and the light

stability of a semiconductor with a big band gap, the dye-sensitized solar cell which made the semiconductor support the sensitizing dye which absorbs the visible light by the side of long wavelength smaller than the band gap of a semiconductor is known. A different place from the wet solar cell using the conventional semiconductor is a photocharge separation process which irradiates a pigment, an electron is excited and an excitation electron moves to a semiconductor from a pigment.

[0011]A dye-sensitized solar cell is related with photosynthesis, and is caught in many cases. Although chlorophyll was considered like photosynthesis as a pigment at the beginning, unlike the natural chlorophyll exchanged for continuously new chlorophyll, there is a problem in respect of stability, and the photoelectric conversion efficiency as a solar cell is not filled with the pigment used for a solar cell to 0.5%, either. It is dramatically difficult to imitate the process of photosynthesis of a nature as it is, and to constitute a solar cell.

[0012]Thus, although a dye-sensitized solar cell obtains a hint from photosynthesis and it is said that it would absorb the visible light of long wavelength, since the electronic transmission machine style became complicated actually, increase of the loss became a problem on the contrary. If the layer which absorbs light is thickened, absorption efficiency can be raised in a solid solar cell. However, about a dye-sensitized solar cell, only the monomolecular layer on the surface can pour an electron into a semiconductor electrode. Therefore, as for the pigment on a semiconductor surface, in order to lose the useless absorption of light, it is desirable to consider it as a monomolecular layer.

[0013]And in order to pour in the electron in the excited pigment into a semiconductor efficiently, having combined with the semiconductor surface chemically is preferred. For example, in order to combine with a semiconductor surface chemically about titanium oxide, it is important that a

pigment has a carboxyl group etc.

[0014]The group of Fujihira and others did the important improvement about this point. They have reported to the magazine Nature that photoelectric current became 10 or more times of the conventional adsorption process in 1977, when the carboxyl group of rhodamine B carries out an ester bond to the hydroxyl group of the SnO_2 surface. It is since this has the pi orbital nearer than the conventional amide bond in which the electron in which the direction of the ester bond absorbed luminous energy within the pigment exists on the surface of a semiconductor.

[0015]However, the electron which is in a conducting zone even if it is able to pour an electron into a semiconductor effectively has a possibility of recombining with the ground level of a pigment, a possibility of recombining with a oxidation reduction substance, etc. Since there was such a problem, photoelectric conversion efficiency was still low in spite of the above-mentioned improvement about electron injection.

[0016]As mentioned above, it is that only the sensitizing dye supported with the monolayer by the semiconductor surface can pour in an electron to a semiconductor as a big problem of the conventional dye-sensitized solar cell. That is, the usable area with which it is smooth in the surface, and the single crystal or polycrystalline semiconductor which were used well [until now] to a semiconductor electrode do not have fine pores in an inside, but sensitizing dye is supported is equal to an electrode area, and there are few holding amounts of sensitizing dye.

[0017]Therefore, when such an electrode is used, the sensitizing dye of the monomolecular layer supported by the electrode can be absorbed 1% or less of incident light also on maximal absorption wavelength, but the utilization efficiency of light gets very bad. In order to heighten light-harvesting power, the trial which makes sensitizing dye a multilayer is also proposed, but sufficient effect is not acquired generally.

[0018]In 1991 the group of Professor GURETSUERU and others of Lausanne Swiss Federal Institute of Technology, The dye sensitizing type solar cell which porosity-ized the titanium oxide electrode, made sensitizing dye support as a means to solve such a problem, and increased the internal surface product remarkably was announced, and it was suddenly brought into the limelight from the possibility of the high photoelectric conversion efficiency and low-manufacturing-cost-izing. Such a solar cell is indicated for example, to Japanese JP.2664196,B. This titanium oxide porous membrane is produced by a sol gel process, membranous porosity is about about 50%, and the nano porous structure which has very high specific surface area is formed. For example, in 8-micrometer thickness, a roughness factor (real area inside the porosity over a substrate area comparatively) amounts also to about 720. When this surface is calculated geometrically, the concentration of sensitizing dye will reach 1.2×10^{-7} mol/cm², and about 98% of incident light will be absorbed very much on maximal absorption wavelength.

[0019]The new dye-sensitized solar cell called this GURETSUERU cell is the feature that the point which absorbed efficiently increase of the fast holding amount of the sensitizing dye by porosity-izing of above-mentioned titanium oxide and sunlight, and sensitizing dye with it developed is big. [a remarkable electron injection speed to a semiconductor and] [quick]

[0020]GURETSUERU and others developed the bis(bipyridyl)Ru(II) complex for the dye-sensitized solar cell. The Ru complex has the structure of general formula ****- X2 bis(2,2'-bipyridyl 4, 4'-dicarboxylate)Ru(II). X is Cl-, CN-, and SCN-. Fluorescence, visible optical absorption, and electrochemical and research systematic about a photooxidation reductive action were done about these, having the performance which boiled markedly ****-(diisocyanate)-bis(2,2'-bipyridyl 4, 4'-dicarboxylate)Ru(II) as a sunlight absorbent and a dye sensitizing agent, and was excellent was shown among these.

[0021]The visible optical absorption of this dye sensitizing agent is the charge transfer transition from metal to a ligand. The carboxyl group of a ligand is directly configurated in surface Ti ion, and forms close electronic contact between a dye sensitizing agent and titanium oxide. It is supposed that re-capture of the electron poured in to the conducting zone of titanium oxide by the dye sensitizing agent in which the electron injection from a dye sensitizing agent to the conducting zone of titanium oxide happened at a very quick speed of 1 pico second or less, and that opposite direction oxidized by this electronic contact is happened to the order of a microsecond. This speed difference produces the directivity of a photoexcited electron, and charge separation is a Reason performed at very high efficiency. And this is the difference from the pn junction solar battery which performs charge separation according to the electric potential gradient of a pn junction surface, and it is prodigal and is the essential feature of a TSUERU cell.

[0022]The composition of a GURETSUERU cell is the sandwiched type cell which enclosed the electrolytic solution containing a redox couple between two conductive glass boards which coated the transparent conducting film of the tin oxide which carried out the fluoride dope. One side of a glass substrate laminates the porous membrane which comprises a titanium oxide ultrafine particle of colloid on a transparent conducting film, makes sensitizing dye adsorb further, and is taken as a work electrode. Another side coats a small amount of platinum on a transparent conducting film, and makes it a counter electrode. A spacer is inserted between two glass substrates and an electrolytic solution is poured into very few crevices between in the meantime using capillarity. The mixed solvent of ethylene carbonate and acetonitrile is used for an electrolytic solution, and it is what made iodination tetra-n-propyl ammonium and iodine the solute, and contains the redox couple of I^-/I^{3-} . The platinum with which the counter

electrode was coated has a catalysis which carries out cathodic reduction of the I_3^- of this redox couple to I^- .

[0023]The principle of operation of a GURETTSUERU cell is not different from the wet solar cell which used the conventional semiconductor fundamentally. However, in every portion of a porous electrode like a GURETTSUERU cell, a photocharge separation response is performed uniformly and efficiently because an electrolyte layer is mainly a liquid. That is, it is because a solution diffuses in porosity uniformly only by dipping a pigment support porous electrode in a solution and an ideal electrochemical interface can be formed.

[0024]However, in spite of saying to be the theoretical efficiency of said GURETTSUERUSERU 33%, the conversion efficiency exceeding size **** is not acquired in 10% after said announcement. One of the cause of this has a problem of the electrical resistance from a dye molecule to a work electrode conducting film. Between ultrafine particles will join together by point contact, and contact resistance increases enlarging a roughness factor rapidly. If thickness is thickened, the electron transfer distance in titanium oxide will become long, and the problem to which the loss by resistance or the loss by recombination becomes large will arise in titanium oxide whose conductivity is lower than metal. That is, since titanium oxide in which electrical conductivity is inferior was used in production of the porous membrane using the ultrafine particle of titanium oxide, it was difficult to improve the electrical conduction of a porous membrane. In the process in which light passes through the inside of a titanium oxide semiconductor, it was accepted as another problem that the passage distance of the light in titanium oxide becomes long, and transmission loss increases.

[0025]Although the trial which mixes a conductive particle in a semiconductor layer and lowers resistance in order to cancel this is made, by this method, the content of titanium oxide will fall and the titanium oxide

surface area per unit volume will decrease. In order to compensate the decrement, if thickness is made to increase, the passage distance of light will become long, and transmission loss will increase. Even if it mixes a conductive particle, there is no change in being an ultrafine particle, and the problem of the contact resistance by point contact is not solved. Thus, it was dramatically difficult to lower resistance.

[0026]

[Problem to be solved by the invention]Therefore, the purpose of this invention is to provide the optoelectric transducer which cancels the fault of such conventional technology, has a low resistance loss and low transmission loss, and can attain high photoelectric conversion.

[0027]

[Means for solving problem]As for said SUBJECT, an electrode is laminated on one field of one substrate at least, A semiconductor layer is laminated on the surface of this electrode, and a counter-electrode is laminated on one field of the substrate of another side. In the optoelectric transducer by which it is arranged so that said semiconductor layer may stand face to face against said counter-electrode, and the electrolyte layer is further allocated between said semiconductor layer and said counter-electrode. At least the part of the optoelectric-transducer components other than said substrate and an electrolyte layer has a slanting columnar structure, and an optoelectric transducer, wherein a crevice exists between these slanting columnar structures is solved.

[0028]In an optoelectric transducer, other than a substrate and an electrolyte layer, depending on for example, an electrode, a semiconductor layer, a counter-electrode, an insulating layer, a catalyst bed, and a case. If at least the part of the components, such as a foundation layer for controlling the adhesion and the crystallinity between electrode layer-boards and between counter electrode layer-boards, is formed with

the slanting vacuum deposition in which a film formation ingredient is entered from an oblique direction to said substrate. These components have a slanting columnar structure, and the crevice originating in the shadowing effect by slanting vacuum evaporation is formed between these columnar structures. As mentioned above, a high energy conversion efficiency cannot be acquired by the method of sintering the conventional metal semiconductor ultrafine particle. Then, as a result of this invention person's etc. repeating examination wholeheartedly, when membranes are formed with slanting vacuum deposition, produce. The holding amount of sensitizing dye was secured by making the crevice originating in a shadowing effect support sensitizing dye, and since it was the slanting columnar structure film which followed the thickness direction and resistance was reduced further, it discovered that a desired energy conversion efficiency was acquired.

[0029]Surface area spreads by existence of a crevice originating in a shadowing effect by slanting vacuum deposition, and since a columnar structure of a metal deposition ingredient serves as a film which followed the counter-electrode side from a conductive layer of a work electrode, a loss of it by contact resistance is lost, and it serves as low resistance. For example, by constituting the surface of a columnar structure from a semiconductor and constituting a center section from a conductive substance, a semiconductor. In order that it can be made necessary minimum thickness which provides a place of photocharge separation and a roughness factor may obtain a high porous membrane, (for example, titanium oxide) can use a high conductive substance of electrical conductivity, and can raise the electrical conductivity of a porous membrane.

[0030]

[Mode for carrying out the invention]A manufacturing method of an optoelectric transducer of this invention is explained concretely, referring to

Drawings. First, a case where an optoelectric transducer is produced using a substrate which does not move is explained. When producing an optoelectric transducer using a fixed board, a vacuum evaporator as shown in drawing 1 is used. The substrate 3 is fixed to the substrate holder 4, and metal of the evaporation source 1 is heated by an electron beam heating, it dissolves, and a component of an ITO film, an electrode layer, a semiconductor layer, an insulating layer, a counter-electrode, an ITO film, etc. is formed one by one on the substrate 3. Various gas is introduced from the gas inlet 2 if needed at the time of membrane formation. Membraneous quality is adjusted with a method of giving energy during membrane formation, a method of performing plasma treatment and a hotpress after membrane formation (ion irradiation by impression of heating with the heater 5, plasma by RF generator 6, and bias potential, and the ion gun 13, etc.), etc. The incidence angle theta over a substrate of a vacuum evaporation steam changes inclination of the substrate 3, and adjusts it with the substrate holder 4 timely. The crevice 21 also becomes larger as this incidence angle theta is generally large. Therefore, although he would like to form membranes at the biggest possible angle, problems, like if an angle will be not less than 80 degrees, film formation efficiency will get very bad, or film strength becomes weak are produced. When theta will be 20 degrees or less, a shadowing effect is not acquired but a crevice stops occurring between columnar structures. Therefore, it is preferred to form membranes in 20 degrees - 80 degrees. However, if the percentage of occupying to all the thickness is 20% or less, even if a not less than 80-degree film exists in membranous [a part of], it will seldom influence to intensity of the whole film. Even if the once vacant crevice 21 forms membranes by 0 degree of incidence angles on it, it is not immediately closed. Therefore, it is satisfactory even if a film of 20 degrees or less exists on a film (20 degrees - 80 degrees). It is satisfactory, if a rate that a film (20 degrees - 80 degrees) occupies on the whole film is large.

enough and at what kind of angle the remaining portion will be formed.

[0031]Thus, if the section of the formed film is observed by TEM etc., as shown in drawing 2, the aslant inclined columnar structure 20 is observable.

If this columnar structure 20 can do one columnar structure from a single crystal, it is not necessarily, but it is an aggregate of a detailed crystal in many cases. As shown in drawing 2, angle-of-inclination theta* of the columnar structure of the film generally formed has much what is risen from theta (it becomes small). There is a tendency to rise more, so that especially the degree of vacuum at the time of membrane formation is low. When it becomes a low vacuum before and behind 1×10^{-3} Torr, in theta, theta* may be around 5 degrees to 50 degrees. Thus, though the columnar structure has risen, the detailed crevice 21 is made between columnar structures. The interval of the crevice 21 should just be sufficient interval required for a sensitizing dye molecule to enter in this crevice. Generally, it is about several nanometers. The interval of the crevice 21 can be adjusted by changing the incidence angle theta of vacuum evaporation metal. Generally, the interval of the crevice 21 also becomes large, so that the incidence angle theta of vacuum evaporation metal is large.

[0032]The surface area of a semiconductor increases by this crevice 21 as well as the case where a semiconductor particulate is sintered, and the quantity of a support pigment can be secured by making a sensitizing dye molecule support here. Evapotranspiration of an electrolysis solution can be stopped to some extent by confining an electrolysis solution in this crevice. Said micropore remains without being closed to the thickness of the grade which has also formed membranes by [as a steam's entering vertically to a substrates face on this]. Therefore, it becomes possible to make micropore (namely, crevice 21) from providing a dummy slanting inclination film also to the film which does not incline aslant in a lower layer.

[0033]As for the height of a columnar structure, it is generally preferred that

it is within the limits of 0.3 micrometer - 10 micrometers. Roughness factor with height of a columnar structure sufficient at less than 0.3 micrometer cannot be acquired. On the other hand, since grain growth arises and the inconvenience of the density of the crevice 21 decreasing arises when the height of a columnar structure is more than 10 micrometers, it is not desirable.

[0034]The surface of the substrate 3 can also make the detailed unevenness 24 exist in the surface, as shown in drawing 2, although it may be smooth. If the detailed unevenness 24 exists in a substrate face, the interval of the crevice 21 will become large and it will become high-density.

[0035]Next, the case where the optoelectric transducer of this invention is produced using long flexible bases, such as a high polymer film and metal foil, is explained, referring to drawing 2. A conductive layer is formed with the vacuum evaporator of drawing 2 on the substrate 3 of long double width. It lets out a flexible base continuously from the **** coiling roll A8 or the *** coiling roll B10, membranes are formed through the peripheral surface of the rotating drum 9 which rotates at the rate of predetermined and which carried out temperature control, and it is rolled round one by one by the *** coiling roll of an opposite hand. Various gas is introduced from the gas inlet 2 if needed at the time of membrane formation.

[0036]The incidence angle over the substrate 3 of a vacuum evaporation steam changes the position of the opening part of a mask, and the position of an evaporation source, and adjusts them timely. Unlike the case of said drawing 1, the incidence angle over the substrate of a vacuum evaporation steam is not kept constant in a thickness direction. When running the *** coiling roll B10 a film from the **** coiling roll A8 (it is henceforth called the direction of A), an incidence angle changes gradually continuously from the incidence angle alpha to the incidence angle beta. Therefore, if the section of the formed film is observed by TEM, as shown in drawing 6, the inclination

of the columnar structure also changes gradually. Between the columnar structures 20, the detailed crevice 21 arises according to a shadowing effect like the case of drawing 2. When running the **** coiling roll A8 a film from the **** coiling roll B10 (it is henceforth called the direction of B), as the inclination of a columnar structure is shown in drawing 5, the inclination changes for reverse.

[0037]Although the rotating drum 9 is used for a run of a substrate in drawing 3, the band conveyor 18 as shown in drawing 6 may be used, and as long as a substrate has heat resistance, membranes may be formed without support as shown in drawing 7.

[0038]Membraneous quality of a film formed by equipment as shown in drawing 3, drawing 6, and drawing 7, a method (it is based on the heater 5 --) of giving energy during membrane formation like a case where the substrate 3 as shown in drawing 1 does not move [and] Ion irradiation by impression of plasma by RF generator 6 and DC power supply 15 and bias potential and the ion gun 13, etc. are adjusted with a method of performing plasma treatment and a hotpress etc., after membrane formation.

[0039]The crevice 21 also becomes larger, as drawing 1 explained and the incidence angles alpha and beta are generally large. Then, although he would like to form membranes at the biggest possible angle, problems, like if the incidence angle beta will be not less than 80 degrees, film formation efficiency will get very bad, or film strength becomes weak are produced. When the incidence angle alpha will be 20 degrees or less, a shadowing effect is not acquired but a crevice stops occurring between columnar structures. Therefore, it is preferred to form membranes in 20 degrees - 80 degrees. However, if the percentage of occupying to all the thickness is 20% or less, even if a not less than 80-degree film exists in membranous [a part of], it will seldom influence to the intensity of the whole film. Therefore, if alpha is 60 degrees or less, in beta, at least not less than 80 degrees of problems will

not arise. Even if the once vacant crevice 21 forms membranes by 0 degree of incidence angles on it, it is not immediately closed. Therefore, if there is not less than 40 degrees beta when membranes are formed with the equipment of drawing 3, at least 20 degrees or less of alpha are satisfactory, and it is satisfactory even if alpha forms membranes to the angle of minus exceeding 0 degree.

[0040]The component of the optoelectric transducer of this invention which can form membranes with equipment as shown in drawing 1, drawing 3, drawing 6, and drawing 7. For example, it is a foundation layer for controlling the adhesion and the crystallinity between electrode layer-boards and between counter electrode layer-boards depending on electrodes other than a substrate and an electrolyte layer, a semiconductor layer, a counter-electrode, an insulating layer, a catalyst bed, and the case, etc.

[0041]Needless to say, a component of an optoelectric transducer of this invention can be formed other than [of applying in ordinary use] slanting vacuum deposition (for example, a method etc.). Such a formation method is publicly known to a person skilled in the art. Therefore, when manufacturing an optoelectric transducer of this invention, a part of the component can be formed with slanting vacuum deposition, other components can also be formed by a method of publicly known common use, and all the components can also be formed with slanting vacuum deposition.

[0042]When forming a component of an optoelectric transducer one by one, about each component, it can also laminate so that it may incline in a uniform direction, or a counter direction can also be made to incline by turns for every component. Therefore, a slope direction of each component can be set up arbitrarily. A columnar structure of each component can also adopt suitably structure shown in drawing 2, drawing 4, and drawing 6.

[0043]If it is the Bex Purdie position method that a substrate can be made to incline to a steamy incidence angle as a forming-membranes method which

causes a shadowing effect, it can be used by any methods. For example, the arbitrary forming-membranes methods, such as vacuum deposition, ion plating, plasma CVD, and a sputtering, can be used.

[0044]As a semiconductor electrode material in the optoelectric transducer of this invention, Cd, Zn, In, Pb, Mo, W, Sb, Bi, Cu, Hg, Ti, A perovskite like the oxide of Ag, Mn, Fe, V, Sn, Zr, Sr, Ga, Si, and Cr, SrTiO₃, and CaTiO₃, Or CdS, ZnS, In₂S₃, PbS, Mo₂S, WS₂, Sb₂S₃, Bi₂S₃, The sulfide of ZnCdS₂ and Cu₂S, CdSe, In₂Se₃, The metal chalcogenide of WSe₂, HgSe, PbSe, and CdTe, other GaAs(es), Si, Se, Cd₂P₃, Zn₂P₃, InP, AgBr, PbI₂, HgI₂, and BiI₃, are preferred. Or the complex which is chosen from said semiconductor and which contains more than a kind at least, For example, CdS/titanium oxide, CdS/Agl, Ag₂S/Agl, CdS/ZnO, CdS/HgS, CdS/PbS, ZnO/ZnS, ZnO/ZnSe, CdS/HgS, and CdS_x/CdSe_{1-x}, CdS_x/Te_{1-x}, CdSe_y/Te_{1-y}, ZnS/CdSe, ZnSe/CdSe, CdS/ZnS, titanium oxide / Cd₂P₃, and CdS/CdSeCd_yZn_{1-y}S and CdS/HgS/CdS are used preferably.

[0045]As a conductor layer by the side of light incidence, conventionally publicly known transparent electric conduction things, such as a kind or two or more sorts of crystalline metallic oxides which were chosen from tin oxide, a zinc oxide, an aluminum oxide, a silicon oxide, 3 indium oxide, 3 strontium oxide, etc., or these multiple oxides, are used. For example, an ITO (Indium tin Oxide) film and a tin-oxide film are the examples of an effective transparent conducting material. If metal particles also have the following light transmittance state, it can be used as a conductive substance used for this invention.

[0046]As for the light transmittance state of the light incidence side conductor layer, it is preferred that the transmissivity of the thin film produced only by the conductive particle is not less than 60%. When a light transmittance state is less than 60%, since the inconvenience of the light volume irradiated by the sensitizing dye supported by the semiconductor

layer decreasing, and sufficient photoelectron no longer being generated arises, it is not desirable.

[0047]As a conductor layer by the side of **** incidence, metal, such as said transparent conducting film and aluminum, Cu, nickel, Ti, Zn, Sn, Au, Ag, Co, and Fe, these alloys, etc. can be used.

[0048]The volume resistivity [of a conductor layer] of below 10⁵ omega-cm is [below 10⁷ omega-cm] 10 or less ohm-cm especially preferably preferably. There is no restriction in particular in the minimum at this time.

[0049]As a substrate in an optoelectric transducer of this invention, transparency, such as a glass plate, a transparent-ceramics board, a polymer board, or a high polymer film, and a translucent board can be used. To a substrate of a side into which light does not enter, opaque boards, such as metal foil, a metal plate, and a ceramics plate, are also usable.

[0050]As a counter-electrode of an optoelectric transducer in this invention, in order to act efficiently as a cathode of an optoelectric transducer, what covered platinum which has a catalysis which gives an electron to an electrolytic reduced form, graphite, etc. on the surface of a counter-electrode is preferred.

[0051]All can be used if it is a pigment of daily use by the conventional dye sensitizing nature optoelectric transducer as sensitizing dye in an optoelectric transducer of this invention. Such a pigment is publicly known to a person skilled in the art. Such sensitizing dye For example, RuL₂(H₂O)₂ type a ruthenium ****-** Aqua bipyridyl complex or ruthenium tris (RuL₃). It is a transition metal complex, metal, nonmetallic phthalocyanine, or porphyrin a ruthenium screw (RuL₁), male *****- tris (OsL₃), and male *****-**** (OsL₂) type etc. As an example, for example, a ****-** (thiocyanato)-N,N-bis(2,2'-bipyridyl 4,4'-dicarboxylate)ruthenium (II) complex, Ruthenium tris (the 2,2'-screw pyridyl 4, 4'-dicarboxylate), Ruthenium cis-***** Irv's (2,2'-screw pyridyl 4,4'-dicarboxylate),

zinc-tetra(4-carboxyphenyl) porphyrin, an iron-hexacyanide complex, phthalocyanine, etc. are mentioned. As organic coloring matter, 9-phenyl xanthene dye, a coumarin series pigment, an acridine dye, triphenylmethane dye, a tetraphenylmethane system pigment, a quinone system pigment, azo dye, an indigo pigment, cyanine dye, a merocyanine system pigment, a xanthene dye, etc. are mentioned.

[0052]As a holding amount of sensitizing dye to a semiconductor layer, what is necessary is just to be in the range of 10^{-8} – 10^{-6} mol/cm², and 0.1 – 9.0×10^{-7} mol/cm² is especially preferred. When a holding amount of the sensitizing dye 19 is less than 10^{-8} mol/cm², a photoelectric-conversion-efficiency improved effect becomes insufficient. On the other hand, when a holding amount of sensitizing dye is 10^{-6} mol/cm² ***, a photoelectric-conversion-efficiency improved effect is saturated and it only becomes uneconomical.

[0053]A method in which a support method of sensitizing dye to a semiconductor layer makes a substrate which made a semiconductor layer laminate on a solution which melted sensitizing dye, for example immersed is mentioned. As a solvent of this solution, if the dissolution of sensitizing dye, such as water, alcohol, toluene, and dimethylformamide, is possible, all can be used. As a dipping former, while making a sensitizing dye solution carry out fixed time immersion of the substrate with an electrode on which a semiconductor layer was made to laminate, it is effective in it to carry out heating flowing back or to impress an ultrasonic wave.

[0054]If a oxidation reduction system composition substance of a couple which consists of an oxidant and a reduced form is contained in a solvent as an electrolyte in an optoelectric transducer of this invention, it will not be limited in particular, but a oxidation reduction system composition substance in which an oxidant and a reduced form have the same electric charge is preferred. A oxidation reduction system composition substance as

used in an oxidation-reduction reaction in this Description means a substance of a couple which exists in a form of an oxidant and a reduced form reversibly. The oxidation reduction system composition substance itself [such] is publicly known to a person skilled in the art. A oxidation reduction system composition substance which can be used by this invention For example, chlorine compound-chlorine, Iodine compound-iodine, bromine compound-bromine, thallium ion (III)-thallium ion (I), Mercury ion (II)-mercury ion (I), ruthenium ion (III)-ruthenium ion (II), Copper-ion (II)-copper-ion (I), iron ion (III)-iron ion (II), Vanadium-ions (III)-vanadium-ions (II), manganic acid ion permanganic acid ion, ferricyanide-ferrocyanide, quinone hydroquinone, fumaric acid-succinic acid, etc. are mentioned. Needless to say, other oxidation reduction system composition substances can also be used.

[0055]A solvent used in order to dissolve an electrolyte has a preferred compound which dissolved a oxidation reduction system composition substance and was excellent in ion conductivity. Although both an aqueous solvent and an organic solvent can be used as a solvent, since a oxidation reduction system composition substance is stabilized more, an organic solvent is preferred. For example, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, Carbonate compounds, such as ethylene carbonate and propylene carbonate, Ester compounds, such as methyl acetate, methyl propionate, and a gamma butyrolactone, Diethylether, 1,2-dimethoxyethane, a 1,3-dioxosilane, Ether compounds, such as a tetrahydrofuran and 2-methyltetra hydra franc, Heterocyclic compounds, such as 3-methyl-2-OKISAZOJI linon and 2-methyl pyrrolidone, Aprotic polar compounds, such as nitril compounds, such as acetonitrile, methoxy acetonitrile, and propionitrile, sulfolane, JIJIME chill sulfoxide, and dimethylformamide, etc. are mentioned. These can also be used independently, respectively, and can also mix and use two or more kinds

together. Especially, especially nitryl compounds, such as heterocyclic compounds, such as carbonate compounds, such as ethylene carbonate and propylene carbonate, 3-methyl-2-OKISAZOJI linon, and 2-methyl pyrrolidone, acetonitrile, methoxy acetonitrile, and propionitrile, are preferred.

[0056]

[Working example]Hereafter, an embodiment illustrates an optoelectric transducer of this invention concretely.

[0057]In mixed liquor (the capacity mixture ratio = 20/1) of water and an acetylacetone containing embodiment 1 surface-active agent, ITO particles (the Mitsui Mining and Smelting make, mean particle diameter of 20 nm) were distributed at concentration about 1 wt%, and slurry liquid was prepared. Next, a dry matter which applied this slurry liquid on the 1-mm-thick glass substrate 30, and was obtained by drying was calcinated in 30 minutes and in the air at 500 **, and 10-micrometer-thick porosity ITO film 31 was formed on a substrate.

[0058]On this layer, using a vacuum evaporator shown in drawing 1, the incidence angle theta was 60 degrees, oxygen gas was introduced by making Ti into an evaporation source, and the 5-micrometer-thick titanium oxide membrane 32 was formed, heating a substrate at 300 ** with an infrared heater. Pigment adsorption treatment was performed having been immersed into a sensitizing dye solution expressed with [Ru(4,4'-dicarboxyl 2,2'-bipyridine)₂(NCS)₂] to this, and flowing back at 80 **, and it was considered as a work electrode.

[0059]Next, on the one more glass substrate 30 in which said ITO film 31 was formed, the incidence angle theta was 0 degree, 20-nm-thick Pt film 34 was formed by having made Pt into the evaporation source, and it was considered as the counterelectrode. Thus, the electrolysis solution 33 (mixed liquor of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide

[0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) is applied, piled up and closed to two produced electrodes. The optoelectric transducer which has section structure as shown in drawing 8 was produced.

[0060] 1-micrometer-thick ITO film 36 was formed having made the alloy of In and Sn into the evaporation source for the incidence angle theta, and introducing oxygen gas on the 100-micrometer-thick polyethylene terephthalate (PET) film 35, using the vacuum evaporator shown in embodiment 2 drawing 1. On this layer, the incidence angle theta was 65 degrees, oxygen gas was introduced by making Zn into an evaporation source, and 5-micrometer-thick ZnO film 37 was formed, irradiating a substrate with ion with the ion gun 13. The ruthenium complex was applied to this as sensitizing dye, and it was considered as the work electrode.

[0061] Next, the incidence angle theta having been 60 degrees, having made Pt into the evaporation source, and introducing oxygen gas on the 1-mm-thick Cu board 41, by making 20-nm-thick Pt film 40, 60 degrees of incidence angles, and Si into an evaporation source, the 1-micrometer-thick silicon-oxide film 39 was formed one by one, and it was considered as the counterelectrode.

[0062] Thus, the electrolysis solution 38 (mixed liquor of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide [0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) is applied to two produced electrodes. The electrolysis solution was made to impregnate in the micropore of a silicon-oxide film, it piled up and closed, and the optoelectric transducer which has section structure as shown in drawing 9 was produced.

[0063] The incidence angle theta on 100-micrometer-thick PET film 42 using the vacuum evaporator shown in embodiment 3 drawing 1 0 degree, 1-micrometer-thick ITO film 43 and the incidence angle theta, introducing oxygen gas by making the alloy of In and Sn into an evaporation source 70 degrees. Introducing oxygen gas by making the alloy of In and Sn into an

evaporation source, 0.1-micrometer-thick ITO film 44 and the incidence angle theta were 60 degrees, oxygen gas was introduced by making Ti into an evaporation source, and the 5-micrometer-thick titanium oxide membrane 45 was formed, impressing high frequency plasma and auto-bias voltage by RF generator 6. The ruthenium complex was applied to this as sensitizing dye, and it was considered as the work electrode.

[0064]1-micrometer-thick ITO film 48 and the incidence angle theta, making an alloy of 0 degree, and In and Sn into an evaporation source for the incidence angle theta, and introducing oxygen gas on the glass substrate 49, next, 60 degrees. Having made Pt into an evaporation source and introducing oxygen gas by making 10-nm-thick Pt film 47, 60 degrees of incidence angles, and Si into an evaporation source, the 1-micrometer-thick silicon-oxide film 46 was formed one by one, and it was considered as a counterelectrode.

[0065]Thus, an electrolysis solution (mixed liquor of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide [0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) is applied to two produced electrodes, All electrolysis solutions were made to impregnate in micropore of the silicon-oxide film 46, it piled up and closed, and an optoelectric transducer which has section structure as shown in drawing 10 was produced.

[0066]It is made to run 30-micrometer-thick PET film 50 in the direction of A using a vacuum evaporator as shown in embodiment 4 drawing 3, alpha-20 degrees of incidence angles and the incidence angle beta were 90 degrees, oxygen gas was introduced by making an alloy of In and Sn into an evaporation source, and 1-micrometer-thick ITO film 51 was formed, having impressed high frequency plasma by RF generator 6, and impressing auto-bias voltage by DC power supply 15. Once rewind this film and it is made to run a film in the direction of A on this layer, and the incidence angle alpha shall be 90 degrees and the incidence angle beta shall be 60 degrees,

Oxygen gas was introduced by making Ti into an evaporation source, and the 5-micrometer-thick titanium oxide membrane 52 was formed, having impressed high frequency plasma by RF generator 6, and impressing auto-bias voltage by DC power supply 15. A ruthenium complex was applied to this as sensitizing dye, and it was considered as a work electrode.

[0067]Next, on 30-micrometer-thick PET film 56, it shall be made to run a film in the direction of A, and alpha=10 degrees of incidence angles and the incidence angle beta shall be 90 degrees, Introduce oxygen gas by making an alloy of In and Sn into an evaporation source, and by RF generator 6 High frequency plasma, 1-micrometer-thick ITO film 55, alpha=20 degrees of incidence angles, and the incidence angle beta shall be 20 degrees, impressing auto-bias voltage by DC power supply 15, 55 degrees and the telophase incidence angle beta having been 80 degrees 20-nm-thick Pt film 54 and the incidence angle alpha by having made Pt into an evaporation source, and introducing oxygen gas by making Si into an evaporation source, the 0.5-micrometer-thick silicon-oxide film 53 was formed one by one, and it was considered as a counterelectrode.

[0068]Thus, an electrolysis solution (mixed liquor of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide [0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) is applied to two produced electrodes, All electrolysis solutions were made to impregnate in micropore of the silicon-oxide film 46, it piled up and closed, and an optoelectric transducer which has section structure as shown in drawing 11 was produced.

[0069]Using a vacuum evaporator shown in embodiment 5 drawing 3, it was made to run the 30-micrometer-thick polyethylene terephthalate (PET) film 57 in the direction of B, alpha=20 degrees of incidence angles and the incidence angle beta were 20 degrees, and 0.1-micrometer-thick Al film 58 was formed by making aluminum into an evaporation source. This film was

once rewound, and the 3-micrometer-thick titanium oxide membrane 59 was formed, having made it run a film in the direction of B, and alpha=10 degrees of incidence angles and the incidence angle beta having been 90 degrees, and introducing oxygen gas by making Ti into an evaporation source on this layer. Subsequently, plasma treatment was performed, having impressed high frequency plasma by RF generator 6, and impressing [made it run a titanium oxide membrane surface in the direction of B,] auto-bias voltage by DC power supply 15. A ruthenium complex was applied to this as sensitizing dye, and it was considered as a work electrode.

[0070]Next, on 30-micrometer-thick PET film 63, it shall be made to run a film in the direction of A, and alpha=10 degrees of incidence angles and the incidence angle beta shall be 10 degrees. Introduce oxygen gas by making an alloy of In and Sn into an evaporation source, and by RF generator 6 High frequency plasma. It is made to run 1-micrometer-thick ITO film 62 and a film in the direction of B, impressing auto-bias voltage by DC power supply 15, and the incidence angle alpha shall be 60 degrees and the incidence angle beta shall be 90 degrees. Having made it run 20-nm-thick Pt film 61 and a film in the direction of A by having made Pt into an evaporation source, and 55 degrees and the telophase incidence angle beta having been the incidence angle alpha 80 degrees, and introducing oxygen gas by making Si into an evaporation source, the 0.5-micrometer-thick silicon-oxide film 60 was formed one by one, and it was considered as a counterelectrode.

[0071]Thus, an electrolysis solution (mixed liquor of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide [0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) is applied to two produced electrodes. All electrolysis solutions were made to impregnate in micropore of the silicon-oxide film 46, it piled up and closed, and an optoelectric transducer which has section structure as shown in drawing 12 was produced.

[0072]It was made to run the 30-micrometer-thick aluminum foil 64 in the direction of B, using a vacuum evaporator shown in embodiment 6 drawing 7, the incidence angle alpha was 65 degrees, the incidence angle beta was 90 degrees, and the 5-micrometer-thick titanium oxide membrane 65 was formed, introducing oxygen gas by making Ti into an evaporation source. Subsequently, a hotpress machine of a wind type performed 500 ** heat-treatment. A ruthenium complex was applied to this as sensitizing dye, and it was considered as a work electrode.

[0073]Next, on 30-micrometer-thick PEN film 69, it shall be made to run a film in the direction of A, and alpha=10 degrees of incidence angles and the incidence angle beta shall be 10 degrees, while introducing oxygen gas by making the alloy of In and Sn into an evaporation source -- 1-micrometer-thick ITO film 68 and a film -- when -- it being made to run in the direction of after [*****] A, and the incidence angle alpha being 60 degrees, and the incidence angle beta being 90 degrees, and, making Pt into an evaporation source -- 20-nm-thick Pt film 67 and a film -- when -- having made it run in the direction of after [*****] A, and 55 degrees and the telophase incidence angle beta having been the incidence angle alpha 80 degrees, and introducing oxygen gas by making Si into an evaporation source, the 0.5-micrometer-thick silicon-oxide film 66 was formed one by one, and it was considered as the counterelectrode.

[0074]Thus, an electrolysis solution (mixed liquor of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide [0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) is applied to two produced electrodes. All electrolysis solutions were made to impregnate in the micropore of the silicon-oxide film 46, it piled up and closed, and the optoelectric transducer which has section structure as shown in drawing 13 was produced.

[0075]3-micrometer-thick Ti film 71 was formed without making it run a film

in the direction of B, and the incidence angle's alpha being 70 degrees, and the incidence angle's beta being 90 degrees, and introducing oxygen gas by making Ti into an evaporation source on 30-micrometer-thick PET film 70, using the vacuum evaporator shown in embodiment 7 drawing 7.

Subsequently, plasma treatment was performed having impressed high frequency plasma by RF generator 6, and impressing [made it run the Ti film surface in the direction of B,] auto-bias voltage by DC power supply 15, and only the columnar structure surface was oxidized. The ruthenium complex was applied to this as sensitizing dye, and it was considered as the work electrode.

[0076]The incidence angle theta on the glass substrate 75 using the vacuum evaporator shown in drawing 1. Next, 0 degree, 1-micrometer-thick ITO film 74 and the incidence angle theta, introducing oxygen gas by making the alloy of In and Sn into an evaporation source 60 degrees, Having made Pt into the evaporation source and introducing oxygen gas by making 10-nm-thick Pt film 73, 60 degrees of incidence angles, and Si into an evaporation source, the 1-micrometer-thick silicon-oxide film 72 was formed one by one, and it was considered as the counterelectrode.

[0077]Thus, an electrolysis solution (mixed liquor of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide [0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) is applied to two produced electrodes, All electrolysis solutions were made to impregnate in the micropore of the silicon-oxide film 46, it piled up and closed, and the optoelectric transducer which has section structure as shown in drawing 14 was produced.

[0078]It is made to run 30-micrometer-thick PET film 76 in the direction of B using the vacuum evaporator shown in embodiment 8 drawing 3, alpha-20 degrees of incidence angles and the incidence angle beta were 90 degrees, oxygen gas was introduced by making the alloy of In and Sn into an

evaporation source, and 1-micrometer-thick ITO film 77 was formed, having impressed high frequency plasma by RF generator 6, and impressing auto-bias voltage by DC power supply 15. It is made to run a film in the direction of A on this layer, and the incidence angle alpha shall be 90 degrees and the incidence angle beta shall be 60 degrees, Oxygen gas was introduced by making Ti into an evaporation source, and 5-micrometer-thick titanium oxide and the film mixture 78 of Ti were formed, having impressed high frequency plasma by RF generator 6, and impressing auto-bias voltage by DC power supply 15. The ruthenium complex was applied to this as sensitizing dye, and it was considered as the work electrode. The rate of titanium oxide and Ti was set to 5:1 by the weight ratio.

[0079]Next, on Ti which applied said ruthenium complex, and the titanium oxide film mixture 78, Make it run a film in the direction of B, and 70 degrees and the incidence angle beta for the incidence angle alpha 90 degrees. The 0.5-micrometer-thick silicon-oxide film 79 is run a film in the direction of A, introducing oxygen gas by making Si into an evaporation source, the incidence angle alpha shall be 70 degrees and the incidence angle beta shall be 90 degrees, while 20-nm-thick Pt film 80 and the incidence angle alpha shall be 70 degrees, the alloy of 90 degrees, and In and Sn is made into an evaporation source for the incidence angle beta by making Pt into an evaporation source and oxygen gas is introduced -- 0.3-micrometer-thick ITO film 81 -- membranes were formed one by one.

[0080]The electrolysis solution (mixed liquor of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide [0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) was applied to this multilayer film, and it was made to impregnate in the micropore of a silicon oxide. Next, in the mixed liquor (capacity mixture ratio = 20/1) of the water and the acetylacetone containing a surface-active agent, ITO particles (the Mitsui Mining and Smelting make, mean particle diameter of 20 nm) were distributed

at concentration about 1 wt%, and slurry liquid was prepared. The dry matter which carried out photogravure spreading of this slurry liquid on the 4-micrometer-thick aramide films 84, and was obtained by drying was heated at 400 ** with the hotpress machine of the wind type, it calcinated in the air, and 10-micrometer-thick porosity ITO film 83 was formed.

[0081]The electroconductive glue 82 was applied, it laid on top of this porosity ITO film 83 with said multilayer film, it was pasted, and the optoelectric transducer which has section structure as shown in drawing 15 was produced.

[0082]In the mixed liquor (capacity mixture ratio = 20/1) of the water and the acetylacetone containing comparative example 1 surface-active agent, ITO particles (the Mitsui Mining and Smelting make, mean particle diameter of 20 nm) were distributed at concentration about 1 wt%, and slurry liquid was prepared. Next, the dry matter which applied this slurry liquid on the 1-mm-thick glass substrate 100, and was obtained by drying was calcinated in 30 minutes and in the air at 500 **, and 10-micrometer-thick porosity ITO film 101 was formed.

[0083]In the mixed liquor (capacity mixture ratio = 20/1) of the water and the acetylacetone containing a surface-active agent, the titanium oxide particle (the product made by Japanese Aerosil, P25, mean particle diameter of 20 nm) was distributed at concentration about 1 wt%, and slurry liquid was prepared. Next, the dry matter which applied this slurry liquid on said ITO film 101, and was obtained by drying was calcinated in 30 minutes and in the air at 500 **, and the 10-micrometer-thick porous-titanium-oxide film 102 was formed on the substrate. Next, pigment adsorption treatment was performed, having been immersed into the sensitizing dye solution expressed with $[\text{Ru}(4,4'\text{-dicarboxy} 2,2'\text{-bipyridine})_2(\text{NCS})_2]$, and flowing back at 80 ** with the substrate which formed this porous-titanium-oxide film 102.

[0084]Next, on the one more glass substrate 106 which formed ITO film 105

like the above, the incidence angle theta was 0 degree, 20-nm-thick Pt film 104 was formed by having made Pt into the evaporation source, and it was considered as the counterelectrode.

[0085]Thus, the electrolysis solution 103 (mixed liquor of ethylene carbonate and acetonitrile containing tetrapropylammonium iodide [0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) is applied, piled up and closed to two produced electrodes. The optoelectric transducer which has section structure as shown in drawing 16 was produced.

[0086]1-micrometer-thick ITO film 108 was formed having made the alloy of 0 degree, and In and Sn into the evaporation source for the incidence angle theta, and introducing oxygen gas on the 100-micrometer-thick polyethylene terephthalate (PET) film 107, using the vacuum evaporator shown in comparative example 2 drawing 1. In the mixed liquor (capacity mixture ratio = 20/1) of the water and the acetylacetone containing a surface-active agent, the titanium oxide particle (the product made by Japanese Aerosil, P25, mean particle diameter of 20 nm) was distributed at concentration about 1 wt%, and slurry liquid was prepared. Next, the dry matter which applied this slurry liquid on said ITO film, and was obtained by drying was calcinated in 30 minutes and in the air at 100 **, and the 10-micrometer-thick porous-titanium-oxide film 109 was formed on the substrate. Next, pigment adsorption treatment was performed, having been immersed into the sensitizing dye solution expressed with $[\text{Ru}(4,4'\text{-dicarboxyl } 2,2'\text{-bipyridine})_2(\text{NCS})_2]$, and flowing back at 80 ** with the substrate which provided this porous-titanium-oxide film.

[0087]Next, on the one more PET board 113 in which ITO film 112 which formed membranes like the above was formed, the incidence angle theta was 0 degree, 20-nm-thick Pt film 111 was formed by having made Pt into the evaporation source, and it was considered as the counterelectrode.

[0088]Thus, the electrolysis solution 110 (mixed liquor of ethylene

carbonate and acetonitrile containing tetrapropylammonium iodide [0.5M] and iodine [0.04M] [capacity mixture ratio =80/20]) is applied, piled up and closed to two produced electrodes. The optoelectric transducer shown in drawing 17 was produced.

[0089]The photoelectric current-voltage characteristic of producing [, respectively]-by said Embodiments 1-8 and comparative examples 1-2 each optoelectric transducer was measured. Using Shimazu Sun Testa XF-180CPS, measurement irradiated the sample cell with the xenon lamp light of 45mW/cm² (1 cm² of irradiation surface products), and measured open end voltage (Voc) and short circuit current density (mA/cm²). Photoelectric conversion efficiency was searched for from these measurement results. The acquired photoelectric conversion efficiency is summarized and shown in the following table 1.

[0090]

[Table 1]

Trial Charge photoelectric-conversion-efficiency (%) embodiment 1 8.9
embodiments 2 5.1 embodiments 3 9.3 embodiments 4 8.2 embodiments 5 7.3
embodiments 6 8.5 embodiments 7 9.2 embodiments 8 9.5 comparative
examples 1 3.5 comparative examples 2 3.1 [0091]As compared with the
comparative examples 1 and 2 which applied the titanium oxide ultrafine
particle, as for the optoelectric transducer of each embodiment by this
invention, photoelectric conversion efficiency rose so that clearly from the
result shown in the aforementioned table 1. It is the result of proving that
the effect which low-resistance-izes the semiconductor layer of an
optoelectric transducer was acquired by the method of forming this
invention.

[0092]

[Effect of the Invention]As explained above, in this invention, at least the part of the components of an optoelectric transducer has a slanting

columnar structure, and establishes a crevice between these slanting columnar structures.

Therefore, the photoelectric conversion efficiency which could make sensitizing dye support in the crevice, and was excellent as a result can be acquired.

By using especially the semiconductor layer of the columnar structure which has a detailed crevice originating in the shadowing effect produced when membranes are formed by the Bex Purdie position method the substrate inclined aslant to the steamy incident direction as a semiconductor layer of an optoelectric transducer. The optoelectric transducer of a low resistance loss can be obtained.

[Translation done.]